Light FCC Gasoline Treating

CDTECH

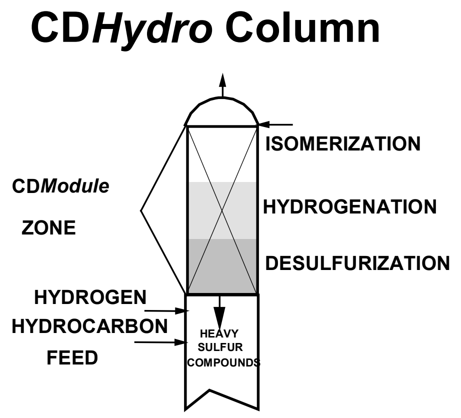


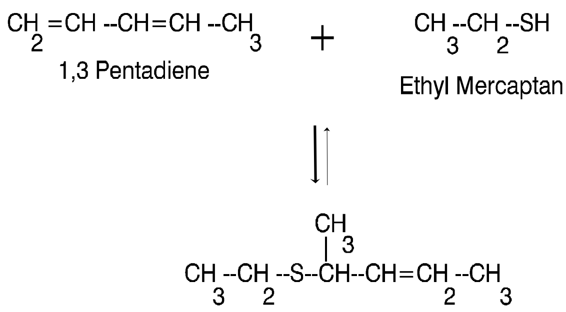
Figure 1

Conventional treating of LCN by extractive caustic systems is not sufficient for future gasoline sulfur levels due to residual disulfides. In addition, if the LCN is sent to an etherification or alkylation unit, removal of diolefins will be required for optimum operation of those processes. An application of CD that addresses all of the above problems has been developed and commercialized. The new application combines selective hydrogenation and distillation and is called the CD*Hydro* process. It is applied by placing selective hydrogenation catalyst in structured distillation packing (CD*Modules*^{SM}) in the top of a depentanizer and adding hydrogen below the catalyst (Figure 1). CD*Hydro* operates at pressures significantly lower than conventional fixed bed reactors. As a result, hydrogen compression is normally not required.

Figure 2

CDHYDRO™

Mercaptan Removal Reaction



$$CH_2{=}CH{-}CH{=}CH{-}CH_3 + CH_3{-}CH_2{-}SH \rightleftharpoons CH_3{-}CH_2{-}S{-}CH(CH_3){-}CH{=}CH{-}CH_3$$

In the bottom of the CD*Module* zone, mercaptans react with diolefins to form olefinic sulfides (Figure 2). These heavy sulfides have higher boiling points than the C_5 fraction and are easily fractionated to the bottom product. Unlike disulfides from caustic sweetening, olefinic sulfides are thermally stable, and therefore do not decompose in the reboiler to cause other problems. The overhead stream is desulfurized without the use of caustic and essentially all sulfur leaves the column with the bottom product. The LCN product typically contains less than 1 ppm mercaptans and can be blended directly into the gasoline pool.

Additional optional hydrotreating functions can be achieved in the CD*Hydro* column. In the upper section of the catalyst, hydrogen reacts with diolefins to selectively produce olefins. The overhead stream is low in diolefins, reducing gasoline gum formation and improving the quality of the LCN for etherification feedstock. Other benefits of selective hydrogenation are reduced RVP and increased octane of the C_5 cut. The double bond isomerization accompanying selective hydrogenation is responsible for both effects. Moving the double bond from the alpha to the beta position on the molecule converts 3-methyl butene-1 to 2-methyl butene-2 or 2-methyl butene-1, and converts pentene-1 to pentene-2. In both cases, the beta-olefin has lower vapor pressure and higher octane than the alpha-olefin (Figures 3 and 4).

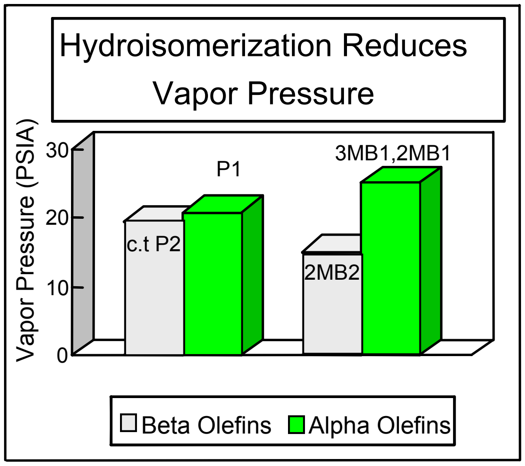


Figure 3

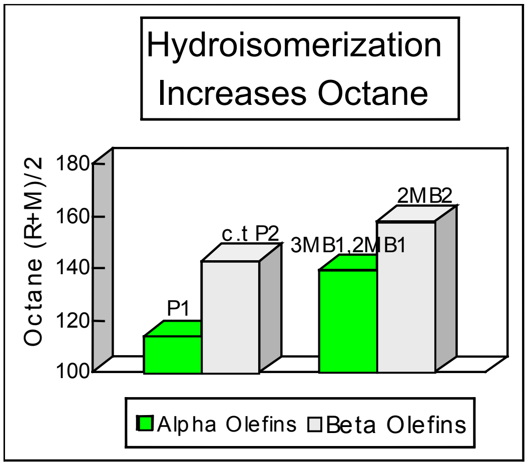


Figure 4

The same types of reactions take place in heavier FCC gasoline components. For example, for the C_6s in the distillate of a dehexanizer;

- Thioetherification reduces the mercaptans in the distillate;
- Selective hydrogenation converts C_6 dienes to olefins;

- Hydroisomerization increases octane by converting alpha olefins to beta olefins.

The octane effect can increase the octane of the full range FCC gasoline by up to 0.5 (R+M)/2.

Another benefit of catalytic distillation is long catalyst life. Conventional fixed bed hydrotreating catalyst gradually loses catalyst activity because the olefinic materials form oligomer intermediates that eventually turn to coke. The coke fouls the conventional fixed bed catalyst by blocking pores. Unlike conventional processes, the distillation environment removes the oligomer intermediate from the catalyst zone before it can form coke. Because the intermediate has a much higher boiling point than the reactants, it can easily be separated by fractionation. As a result the catalyst zone stays very clean and maintains high catalyst activity for much longer times than conventional fixed bed catalysts.

Currently, there are five CD*Hydro* units which were built to process FCC gasoline feedstock:

Refinery	**Location**	**Start-up**
Ultramar Diamond Shamrock	Sunray, Texas	1994
Equilon	Martinez, California	1994
Pennzoil	Shreveport, Louisiana	1995
Irving Oil	St, John, New Brunswick	2000
Texaco	Pembroke, UK	2002

No loss of catalyst activity has been observed for the original charge in any of these units, nor has any regeneration has been performed.

Conclusions

The CD*Hydro* process treats light catalytic naphtha to remove mercaptans and diolefins while increasing octane. It eliminates the need for separate caustic treating and selective hydrogenation units. It also eliminates the make-up and spent caustic requirements. It has very long catalyst life, eliminating the need for catalyst regeneration or replacement through the full FCC turnaround cycle. Coupled with the CD*HDS* process, the CD*Hydro* process can enable refiners to produce ultra low sulfur gasoline at low cost and high reliability.